

# ELECTROCHEMICAL PERFORMANCE TESTING

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# OVERVIEW

## Timeline

- Facility established: 1976
- End: Open – this is an on-going activity to test/validate/document battery technology as technologies change and mature

## Budget

- DOE Funding FY16: \$1.8 M
- FY15: \$2.0 M
- FY14: \$2.3 M

## Barriers

- Performance (power and energy densities)
- Cycle life (1,000-300,000 depending on application)
- Calendar life (15 y)
- Low-temperature performance

## Collaborations

- US battery developers
- Idaho National Laboratory, Sandia National Laboratories
- CATARC (China)
- Purdue Univ., Battery Innovation Center

# RELEVANCE

## Objective

- To provide DOE and the USABC an independent assessment of contract deliverables and to benchmark battery technology not developed under DOE/USABC funding
- To provide DOE and the USABC a validation of test methods/protocols
- To develop methods to project battery life and to use these methods on test data

## Approach

- Apply standard, USABC testing methods in a systematic way to characterize battery-development contract and benchmarking deliverables
- Characterize cells, modules and packs in terms of:
  - Initial performance
  - Low temperature performance/Cold cranking
  - Cycle life
  - Calendar life
- Compare test results to DOE/USABC goals
- Adapt the test facility hardware and software
  - to accommodate programmatic need
  - to accommodate the unique needs of a given technology and/or deliverable

# PROGRAM MILESTONES

Milestone	Date	Status
Submit quarterly reports to DOE and USABC	12/31/15	Complete
Submit quarterly reports to DOE and USABC	3/31/16	Complete
Submit quarterly reports to DOE and USABC	6/30/16	On track
Submit quarterly reports to DOE and USABC	9/30/16	

# TECHNICAL ACCOMPLISHMENTS: PROGRESS AND RESULTS – TESTING CONTRACT DELIVERABLES

- Test deliverables are mostly cell-oriented and include developments in
  - Lithium-ion battery chemistry (graphite anodes)
  - Silicon anodes
  - Battery recycling
  - Lithium metal anodes
  - Separators
  - Advanced cell chemistries (beyond Li-ion)
- Deliverables are characterized in terms of initial capacity, resistance, energy and power. They are then evaluated in terms of cycle and calendar life for the given application
- Results are used to show progress toward meeting DOE/USABC initial commercialization goals

# PROGRESS AND RESULTS – TESTING CONTRACT DELIVERABLES

Developer	Sponsor	Level	Quantity	Rated capacity, Ah	Application	Status
JCI	USABC	Cell	9	27	PHEV-20	on-going
	DOE FOA	Cell	18	15	PHEV-20	on-going
	DOE FOA	Cell	4	15	PHEV-20	on-going
	DOE FOA	Cell	23	3	PHEV-20	on-going
	DOE ARRA	Cell	18	6.8	HEV	complete
Leyden	USABC	Cell	30	2.2	12-V S/S	on-going
	USABC	Cell	20	20	12-V S/S	complete
	USABC	Pack	3	40	12-V S/S	complete
Maxwell	USABC	Cell	6	0.357	12-V S/S	on-going
	USABC	Module	15	40	12-V S/S	on-going
	USABC	Cell	15	0.357	12V S/S	on-going
24-M	USABC	Cell	6	0.79	EV	on-going
	DOE	Cell	10	4.3		on-going
Xerion	USABC	Cell	21	0.92	PHEV-20	on-going
Optodot	DOE FOA	Cell	9	2.1	EV	complete
3M	DOE FOA	Cell	18	1.7	EV	complete
	DOE FOA	Cell	6	2.7	EV	complete
	DOE FOA	Cell	15	2.7	EV	complete
	2013 ABR	Cell	10	2.1	EV	complete
	2013 ABR	Cell	12	2.88	EV	on-going
Navitas	DOE FOA	Cell	24	14	EV	on-going
		Cell	13	2+4	EV	complete
Tiax	2013 ABR	Cell	13	1.8	EV	on-going
ANL (J. Zhang)	DOE	Cell	15	0.16	EV/PHEV	on-going
Seeo	DOE	Cell	4	11	EV	on-going
	DOE	Cell	2	2.2	EV	complete
	USABC	Module	3	11	EV	complete
LG Chem	DOE	Cell	10	25.9	PHEV-40	on-going
XALT	USABC	Cell	24	95	EV	on-going
Wildcat	DOE	Cell	20	6 1.7	EV	on-going

- Test deliverables come from many developers

# PROGRESS AND RESULTS – COLLABORATIVE US/CHINA PROTOCOL COMPARISON

- Battery testing is a time-consuming and costly process
- There are parallel testing efforts, such as those in the US and China
- These efforts may be better leveraged through international collaboration
- The collaboration may establish standardized, accelerated testing procedures and will allow battery testing organizations to cooperate in the analysis of the resulting data
- In turn, the collaboration may accelerate electric vehicle development and deployment
- There are three steps in the collaborative effort

Step	Status
Collect and discuss battery test protocols from various organizations/countries	Complete
Conduct side-by-side tests using all protocols for a given application, such as an EV	Complete
Compare the results, noting similarities and differences between protocols and test sites	Complete; open-literature paper published

# CONDUCT SIDE-BY-SIDE EXPERIMENTS

- A test plan based on an EV application was written and agreed to
- Commercially-available batteries based on  $\text{LiFePO}_4$  and carbon were procured. The batteries were distributed to ANL, INL\* and CATARC (China)
- Initial similarities and differences
  - The US cycle-life aging protocol consists of a dynamic, constant-power profile and constant-current charging
  - The Chinese cycle-life aging protocol consists of constant-current discharges and charges
  - USABC Reference Performance Test consists of 2 capacity cycles, peak power pulse test at 10% DOD increments and full DST cycle. The cells are characterized using these performance tests every 50 cycles
  - China Reference Performance Test consists of 1 capacity cycle and 10 second discharge pulse at 50% DOD. The performance of the cells were characterized using these performance tests every 25 cycles
  - Both cycle-life protocols terminate discharge at 80% DOD

\*Jon Christophersen, Taylor Bennet



# COMPARING THE PROTOCOLS SHOWS...

	USABC	China
DOD (Energy) Window	0-80% DOD	0-80% DOD
Temperature	25 °C	25 °C
Capacity measurement rate	C/3	C/3
End of Test criteria	80% degradation	80% degradation
Cycle Type	Dynamic, Power based	Constant-current
Power Capability Measurement	Peak Power Pulse Estimation at 80% DOD	Pulse Power Density at 50% DOD
Pulse duration	30 seconds	10 seconds
Pulse Current	75A	225A
RPT Frequency	50 cycles (10.5 days)	24 cycles (6 days)
RMS power of cycle	50-51 W	12-13 W
RMS current of cycle	15-16 A	3.5-4 A
Average Voltage of cycle	3.17V fading over time	3.27V without fading
Energy throughput of cycle	27 Wh	19.5 Wh

# DISTRIBUTION OF CELLS AND INITIAL CHARACTERIZATION

- Since the QC/T method uses resistance at 50% DOD (10 s) as a metric, resistance from the USABC method was calculated at 50% DOD (10 s), 50% DOD (30 s), 80% DOD (10 s) and 80% DOD (30 s) to facilitate comparison

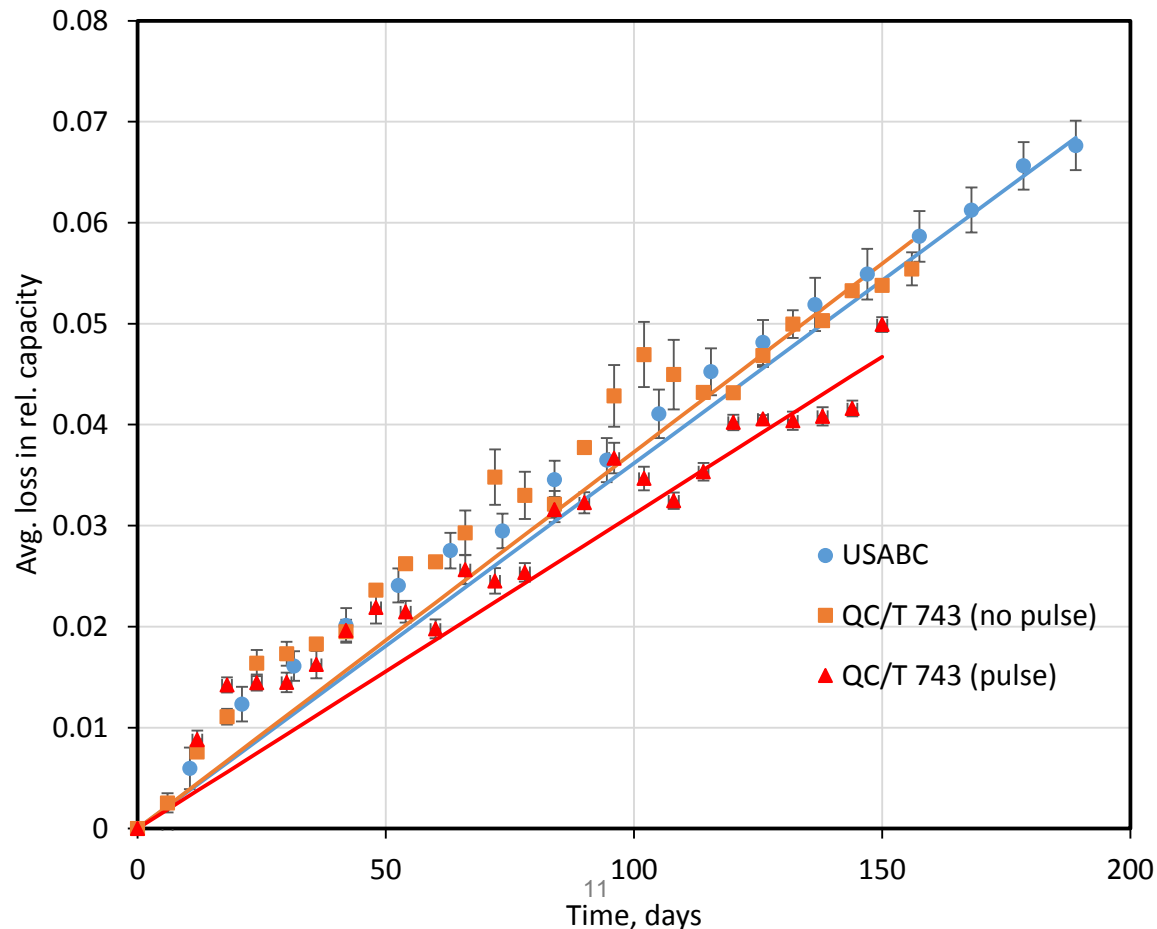
Average performance parameters measured by using two protocols.

Protocol	Parameter	Average value (s.d.)
USABC	C/3 capacity, Ah	7.46 (0.09)
	Resistance at 50% DOD (10 s), mΩ	3.97 (0.04)
	Resistance at 50% DOD (30 s), mΩ	4.71 (0.04)
	Resistance at 80% DOD (10 s), mΩ	5.41 (0.10)
	Resistance at 80% DOD (30 s), mΩ	7.45 (0.12)
QC/T 743 (no pulse)	C/3 capacity, Ah	7.74 (0.06)
QC/T 743 (pulse)	C/3 capacity, Ah	7.62 (0.12)
	Resistance at 50% DOD (10 s), mΩ	3.46 (0.03)

- Differences in pulse width and magnitude affected results
  - Degree of electrode polarization and mass/charge transfer effects

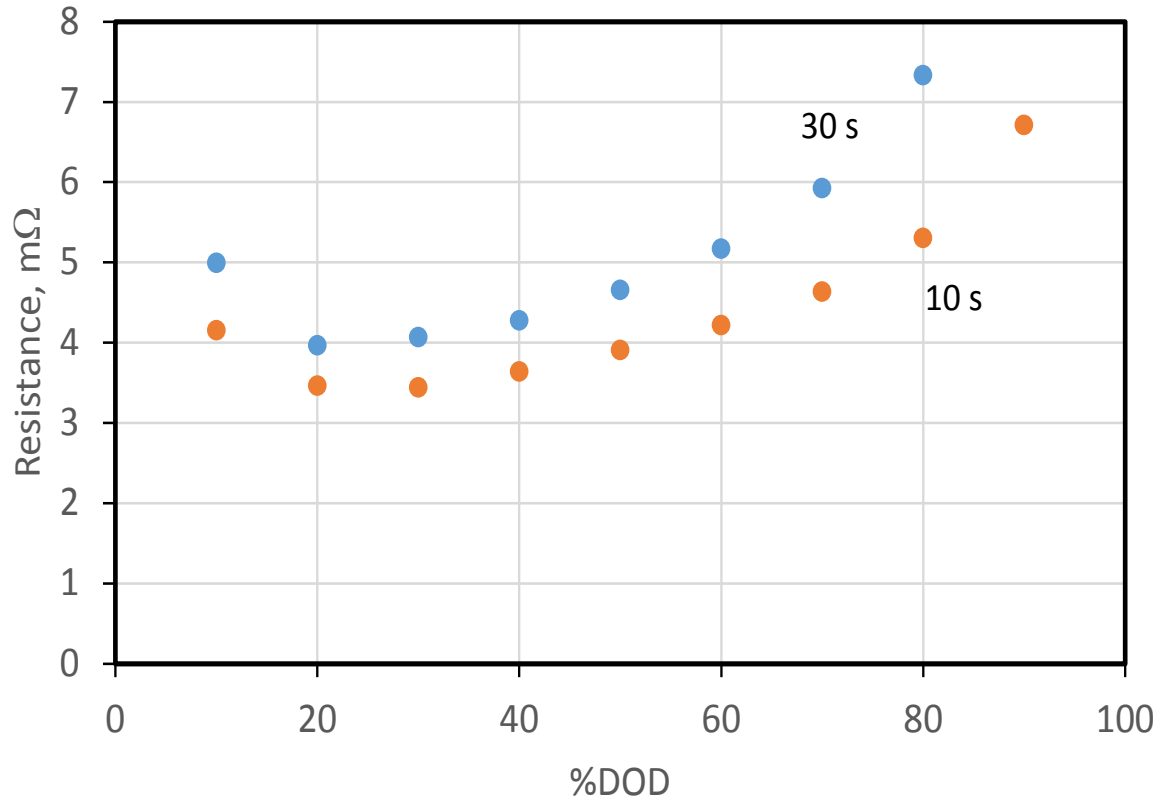
# CAPACITY FADED WITH CYCLING

- Average loss in cell capacity appeared to be linear with time and increased at the same approximate rate, within experimental error ( $\pm 2\sigma$ )



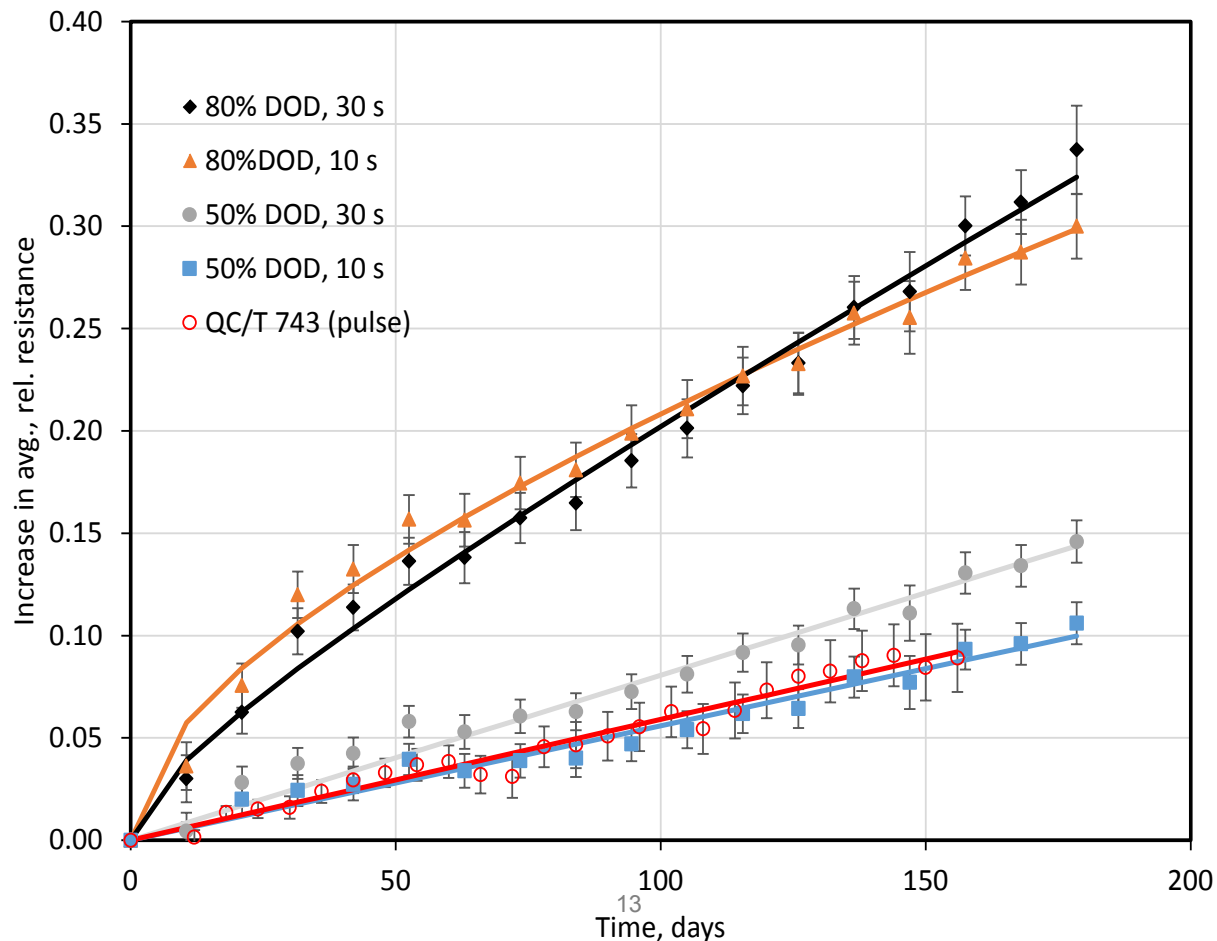
# CELL RESISTANCE: %DOD AND PULSE WIDTH

- Using data from USABC protocol, as expected, the 10-s values were lower than the 30-s ones



# CELL RESISTANCE INCREASED WITH CYCLING

- %DOD and pulse-width affect apparent mechanism of resistance increase
  - 50% DOD, 10- and 30-s: resistance increase follows  $a \cdot t$  rate law
  - 80% DOD, 10- and 30-s: resistance increase follows  $a \cdot t + b \cdot t^{1/2}$  rate law



# APPARENT RESISTANCE INCREASE MECHANISM IMPACTS ESTIMATED LIFE

- 30% increase in resistance was used as end-of-life metric

Protocol and metric parameters	Estimated life, days
USABC (50% DOD, 10 s)	536.67
USABC (50% DOD, 30 s)	372.21
USABC (80% DOD, 10 s)	178.50
USABC (80% DOD, 30 s)	168
QC/T 743 (pulse)	510

- There was a large difference in estimated life using usual %DOD and pulse widths between the USABC and the QC/T 743 protocols
- With the right combination of tests and metric points, the two protocols produce similar results
- The results described here provide a starting point for a discussion between the two groups

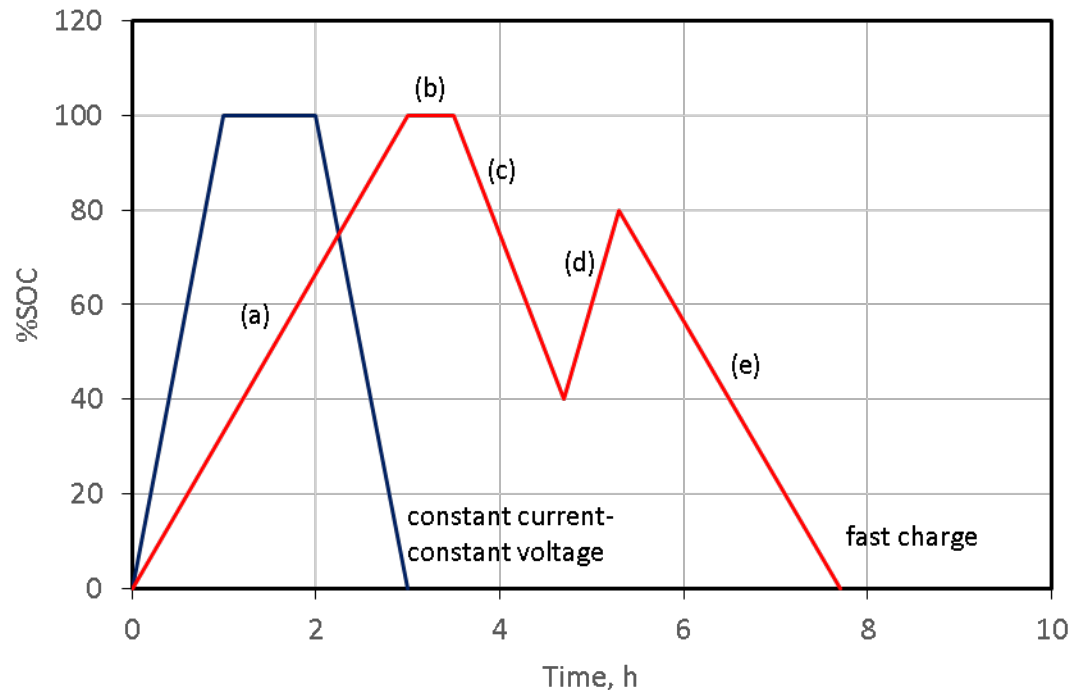
# PROGRESS -- PROTOCOL VALIDATION/EFFECT OF FAST CHARGE

- With further vehicle electrification, customers would desire battery charging to take the same amount of time as refueling an ICE does at a service station. This does not have to be a full charge
- The Fast Charge Test in the USABC EV Manual<sup>2</sup> determines the impact of charging a battery from 40 to 80% SOC at successively faster rates, starting from about twice the overnight rate. Since the manual was written for Ni/MH technology, the ideas were adapted for the higher-performing, lithium-ion cells
- Commercial, 18650-sized lithium-ion cells, consisting of NMC-based chemistry, were chosen

<sup>2</sup>Electric Vehicles Battery Test Procedures Manual, Rev. 2, January 1996.

# COMPARE FAST-CHARGE AND CONSTANT-CURRENT PROFILES

- Two tests
  - Fast-charge (FC) and constant-current (CC)
  - RPTs (C/1 capacity and EV Peak Power Test) every 100 cycles

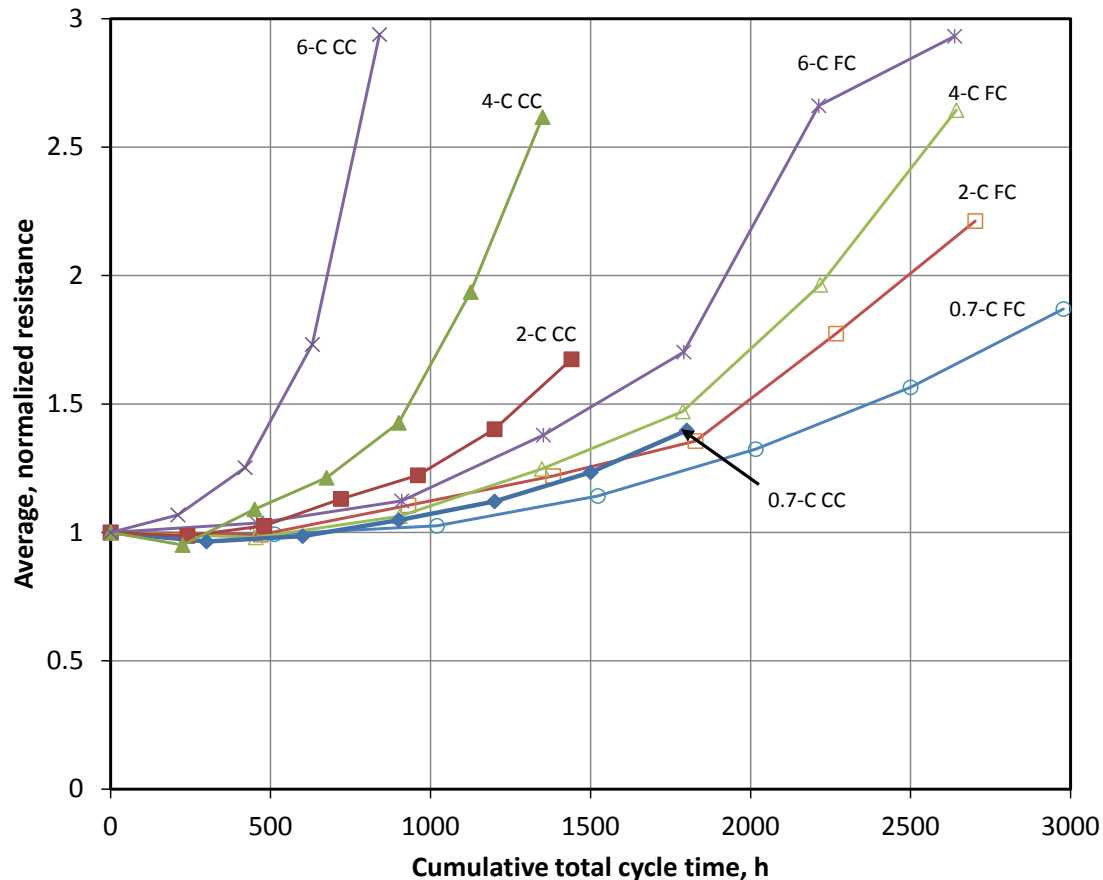


- The segments represent (a) C/3 charge to 100% SOC; (b) 30-min rest; (c) C/3 discharge to 40% SOC; (d) fast charge to 80% SOC; and (e) C/3 discharge to 0% SOC. The fast-charge step shown in this particular profile used twice the simulated overnight rate, 2C/3.



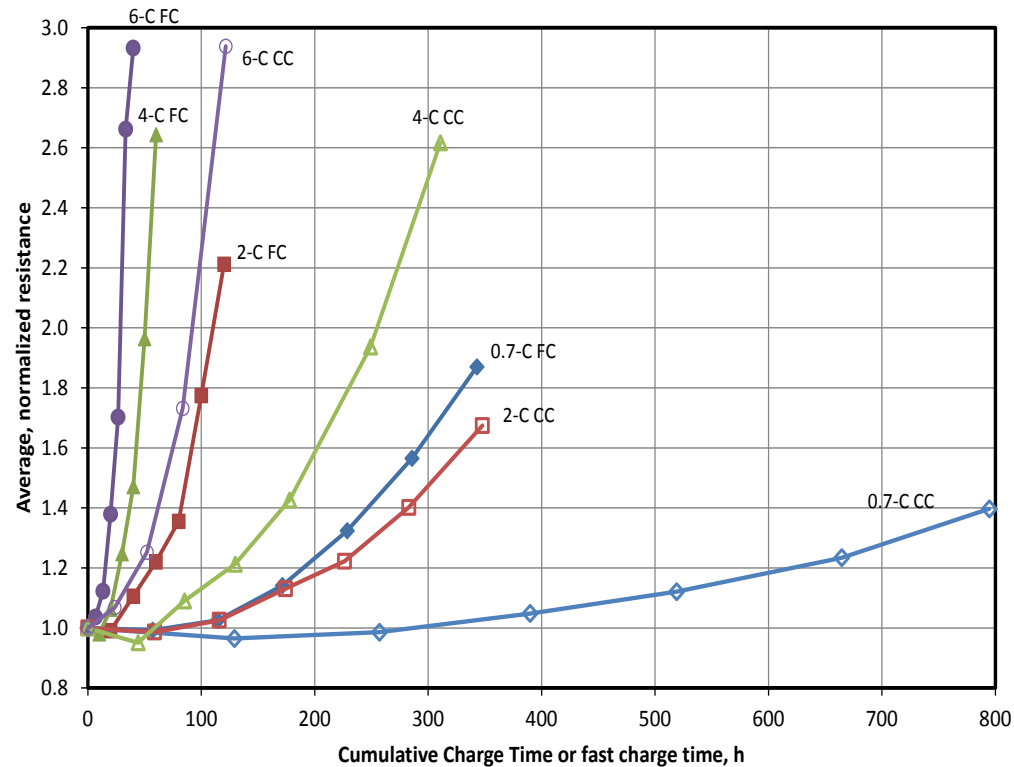
# CELL RESISTANCE CHANGED DURING THE TESTS

- Since time base is ambiguous, how should the resistance data be presented?
  - Total cycle time or cumulative charge time



- CC data appears to show faster resistance increase

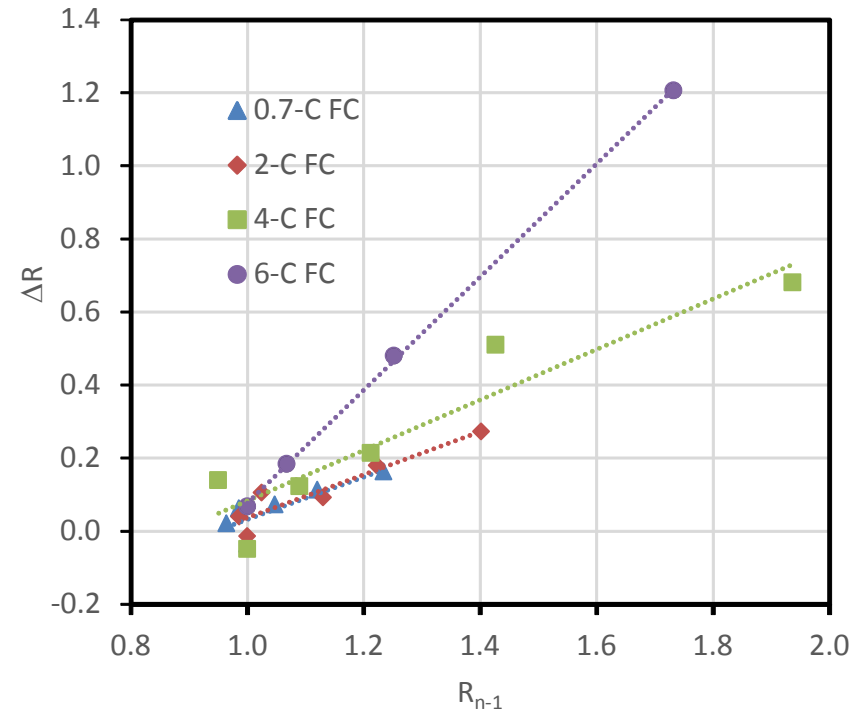
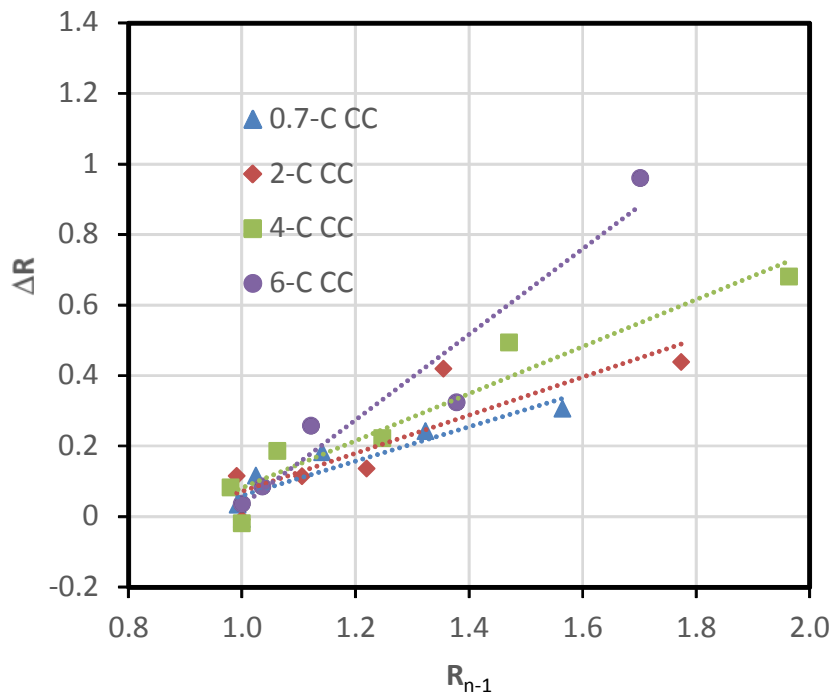
# CELL RESISTANCE CHANGED DURING THE TESTS (CONTINUED)



- Here, FC results appear to increase faster than CC, the direct opposite of the previous plot

# PLOTTING $\Delta R$ VS. $R_{N-1}$ REMOVES AMBIGUITY

- From the slopes of lines, fast-charging causes resistance to rise faster



# ...WHICH IS CONSISTENT WITH POST-TEST RESULTS

- More delamination seen on the anodes of FC cells



6C



4C



2C



0.7C



0.7C



2C



4C



6C

# SUMMARY AND FUTURE WORK

## ■ Summary

- Hardware deliverables from many sources have been tested at Argonne and continue to be evaluated for a variety of vehicle applications
- This testing directly supports DOE and USABC battery development efforts
- The US/China Protocol Comparison has shown
  - There are similarities and differences in the test protocols
  - With similar metric points, the results are comparable
- The results of the fast charge test have shown that cell heating at high charge rates is the main cause of resistance increase. This result may have practical implications

## ■ Future Work

- Continue to support the DOE and USABC battery development efforts by performing unbiased evaluations of contract deliverables, using standardized test protocols
- Start the next experiment with the Chinese on fast-charging LiFePO<sub>4</sub>-based cells

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**THANK YOU.**